AFRL-AFOSR-UK-TR-2011-0025

DOPING, IONIC CONDUCTIVITY AND PHOTOTHERMAL STABILITY OF FUNCTIONALIZED DNA FOR SOLAR ENERGY CONVERSION AND ELECTROCHROMIC APPLICATIONS

Ileana Rau

University POLITEHNICA of Bucharest
Faculty of Applied Chemistry and Materials Science
Department of General Chemistry
1 Polizu Street
Bucharest, Romania 011061

EOARD GRANT 10-3073

June 2011

Final Report for 16 June 2010 to 15 June 2011

Air Force Research Laboratory
Air Force Office of Scientific Research
European Office of Aerospace Research and Development
Unit 4515 Box 14, APO AE 09421

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From – To)*
17-06-2011	Final Report	16 June 2010 – 15 June 2011

4. TITLE AND SUBTITLE

DOPING, IONIC CONDUCTIVITY AND PHOTOTHERMAL STABILITY OF FUNCTIONALIZED DNA FOR SOLAR ENERGY CONVERSION AND ELECTROCHROMIC APPLICATIONS

5a. CONTRACT NUMBER

FA8655-10-1-3073

5b. GRANT NUMBER

Grant 10-3073

5c. PROGRAM ELEMENT NUMBER

61102F

6. AUTHOR(S)

Professor Ileana Rau

5d. PROJECT NUMBER

5d. TASK NUMBER

5e. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University POLITEHNICA of Bucharest
Faculty of Applied Chemistry and Materials Science
Department of General Chemistry
1 Polizu Street
Bucharest, Romania 011061

8. PERFORMING ORGANIZATION REPORT NUMBER

N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

EOARD
Unit 4515 BOX 14
APO AE 09421

10. SPONSOR/MONITOR'S ACRONYM(S)

AFRL/AFOSR/RSW (EOARD)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

AFRL-AFOSR-UK-TR-2011-0025

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited. (approval given by local Public Affairs Office)

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Biopolymers DNA and collagen were studied for their practical application in photonics and electronics. They were functionalized with optically active chromophores. Additionally DNACTMA complexes is known for excellent optical properties and solubility in other solvents than water, the only solvent of DNA. Thermal and photodegradation of thin films of two biopolymers and the stability of embedded chromophores were studied at room and elevated (85 deg C) temperatures as well as under UV irradiation. Thin films were obtained by spin coating of corresponding solutions on glass substrates. Fluorescence of active molecules was also studied as a function of matrix and fluorophore concentration. The optical damage threshold for several systems was also determined and it was found to be larger than in synthetic chromophores. Practical application of DNA as a solid polyelectrolyte was demonstrated in electrochromic cell acting as a smart window structure.

15. SUBJECT TERMS

EOARD, electrochromic, biopolymer, functionalized DNA, photostability, fluorescence

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18, NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Randall Pollak, Lt Colonel, USAF
UNCLAS	UNCLAS	UNCLAS	SAR	31	19b. TELEPHONE NUMBER *(Include area code)* +44 (0)1895 616115

RESEARCH REPORT

Period 16.06.2010 – 15.06.2011

Research project: DOPING, IONIC CONDUCTIVITY AND PHOTOTHERMAL STABILITY OF FUNCTIONALIZED DNA FOR SOLAR ENERGY CONVERSION AND ELECTROCHROMIC APPLICATIONS

EOARD PROJECT FA8655-10-1-3073

Table of Contents

1. Introduction

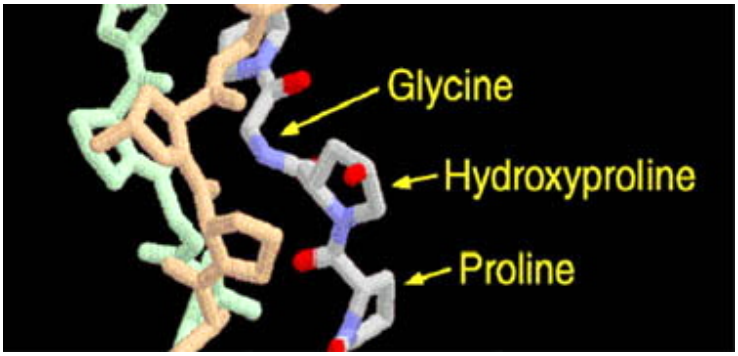
DNA and the another biopolymer collagen are very interesting materials, with a high potential for application in photonics and in electronics, as it shows the recent studies of J. Grote from US AF WPRL, Dayton, Ohio and coworkers [1,2,3,4] . They are renewable and biodegradable materials, recovered from waste in food industry (fruits, animal and fish meat waste) and it is expected that they will replace synthetic polymers, known as having a very long degradation time (eg. polyethylene about 400 years). However the biopolymers, similarly as most of synthetic polymers, are optically and electronically inactive materials. Therefore in order to obtain defined properties they have to be functionalized with active molecules, procuring a well defined property, like good thin film formation ability, excellent light propagation properties, good charge mobility, etc. depending on targeted applications.

In this project we focused our studies on functionalization of DNA and of collagen with active molecules and thin film processing, their photostability in view of their further application in electronics and photonics as all optical switching elements, bioleds, optical memories, light amplifies, electro-optic modulators, etc. We have particularly addressed the very important point for the practical application of these materials, not studied previously, which is the photostability of these materials. If they have to work in photonic systems they have to exhibit an excellent stability in time and at the temperature operation range, in practical devices. The interest for biopolymers arises from:

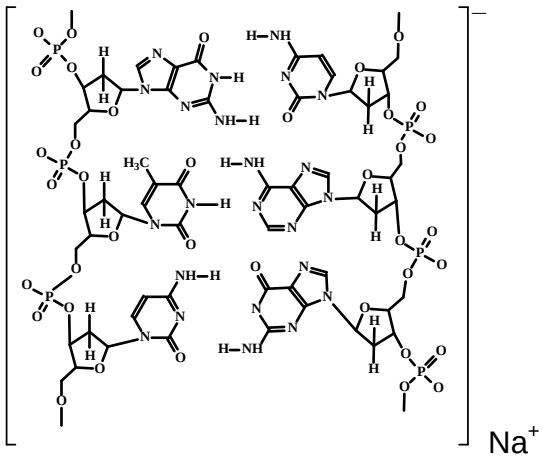
Renewable, coming from waste of food industry

Biodegradable

Peculiar, chiral structure, allowing chemical modification, functionalization, or even multiple functionalization and easy doping. In fact, collagen exhibits a triple and DNA a double helix structure with lot of free space, as it shows Fig1. Also doping can be made inside the helix, or between the base pair stakes (intercalation), a potentially interesting property for protection of the active, dipolar molecules from aggregation, which is one of the main problems when working with functionalization of synthetic polymers.



(a)



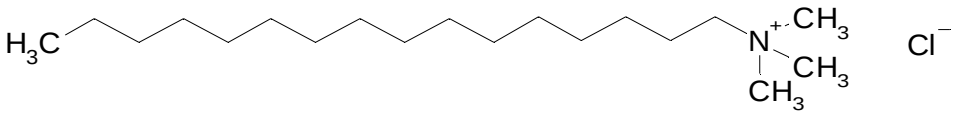
(b)

Fig. 1. Chemical structures of collagen (a) and DNA (b). Left hand side shows the macroscopic spiral structure (triple helice in collagen and double in DNA) whereas the right hand site the elementary cell, respectively

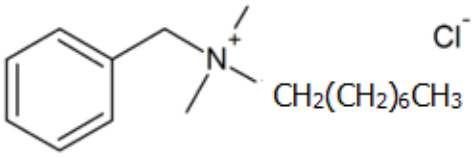
.

II. Functionalization of DNA and doping

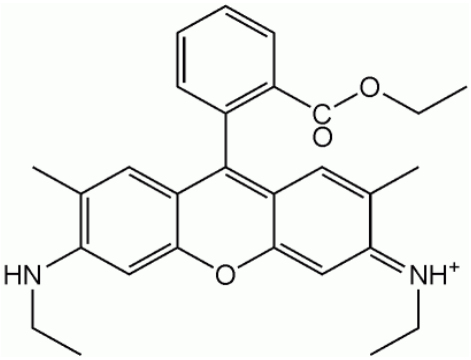
Pure DNA is soluble in water only. It limits its application in devices because of technological limitations. Moreover it undergoes a denaturation process at temperatures about 90 °C, consisting on change from double stranded helical structure to the single stranded one. A big process in processing of DNA and its practical utilisation was realized after discovery that it reacts chemically with some surfactants or lipids. The chemical structures of studied chromophores are given in Fig. 2.



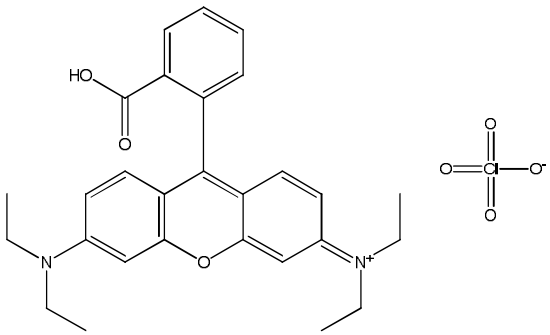
CTMA



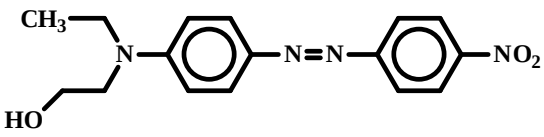
BA



Rhodamine 590



Rhodamine 610



Disperse Red #1

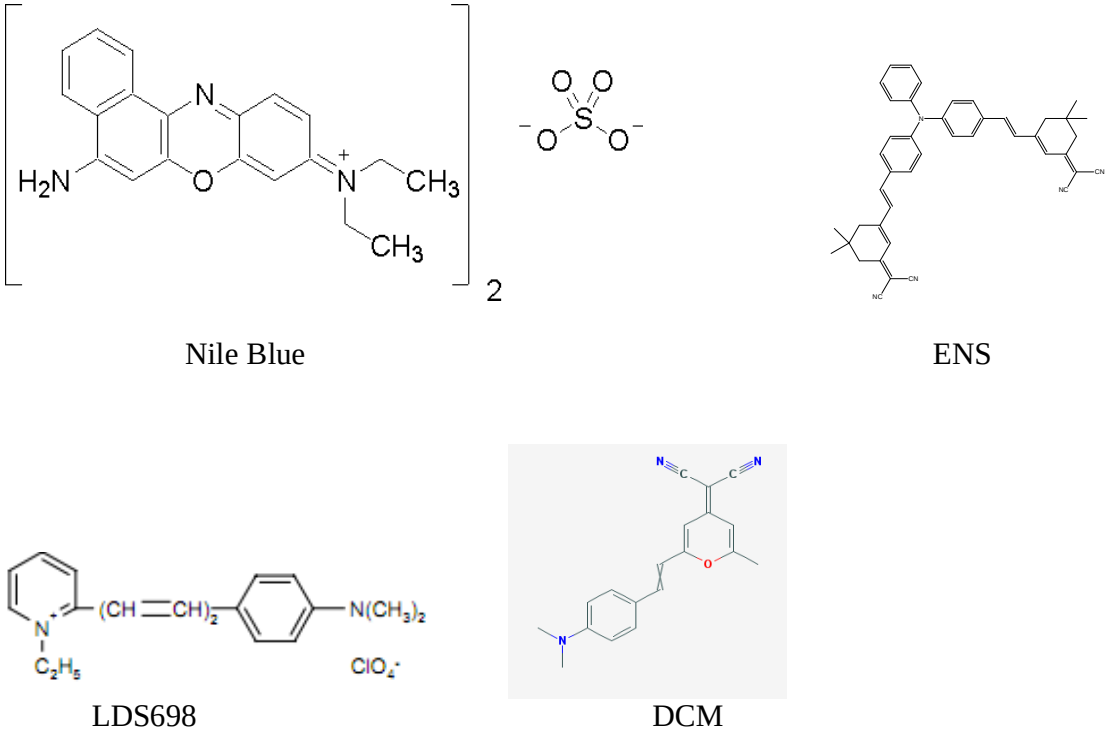


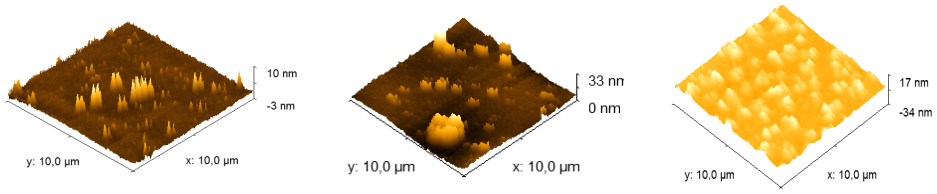
Fig. 2. Chemical structures of doping molecules used. All chromophores are commercially available except ENS which was originally synthesized by ENS Lyon (France).

III. Thin film processing

The physical studies were performed either on solution, thin films or on both: solutions and thin films. Thin films were obtained by spin coating on carefully cleaned glass or silica substrates, depending whether the studies were performed in UV or not. The glass is known to exhibit the optical transmission cut-off at ca. 300 nm. In most cases good optical quality thin films were obtained.

For solutions the spectroscopic grade solvents were used. The spin coating machine was Laurell – Model WS – 400B – 6NPP/LITE with possibility of operating at chemically inactive atmosphere (argon or nitrogen).

Figure 3 shows AFM images of thin films of DNA-CTMA-DR1 complexes as function of concentration. This molecule is acentric with a large ground state dipole moment. The strong dipole-dipole interaction leads to molecules aggregation, a highly undesirable effect leading to the loss of light propagation properties because of light scattering by the aggregates..



DNA-CTMA-DR1 5% DNA-CTMA-DR1 10% DNA-CTMA-DR1 20%

Fig. 3. AFM images of DNA-CTMA-DR1 thin films with different active chromophore concentration.

This aggregation process is clearly seen in Fig. 3, showing the AFM images of DNA-CTMA-DR1 thin films with different active chromophore concentrations. Small aggregates appear already at 5 w% doping level and they increase with DR1 concentration, covering at 20% DR1 content the whole thin film surface.

The measured thin film absorption spectra for studied systems, at different dopant concentrations, are displayed in Figs. 4 - 9. The spectra were measured for solid thin films and were obtained with JASCO UV – VIS - NIR spectrophotometer, model V 670.

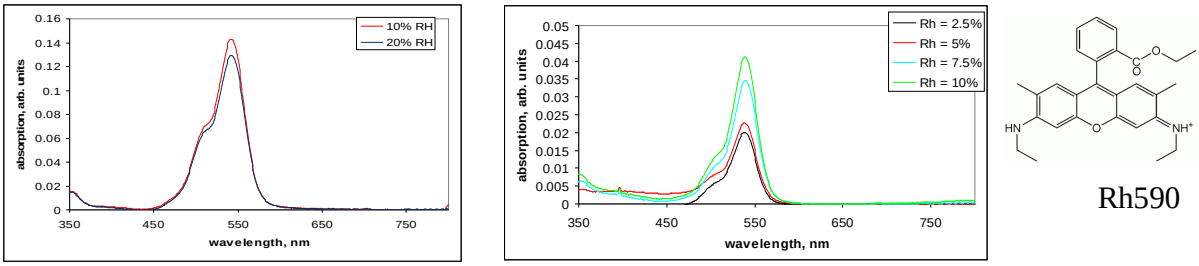
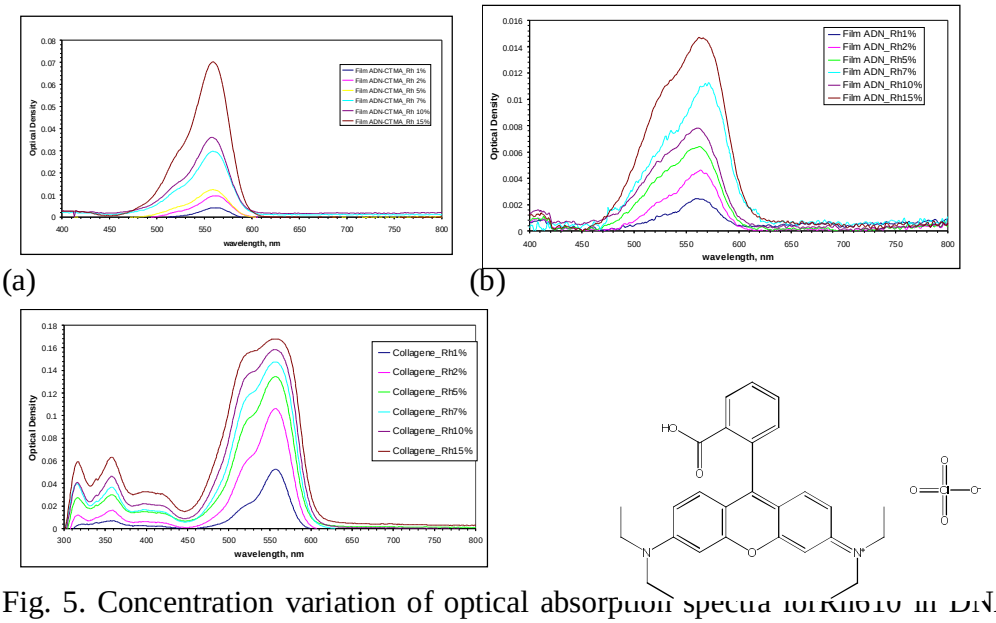
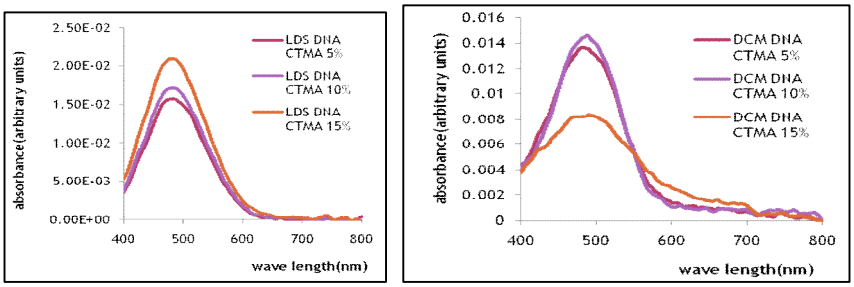


Fig. 4. Absorption spectra of Rh590 in DNA (a) and in collagen (b) for different dopant concentrations



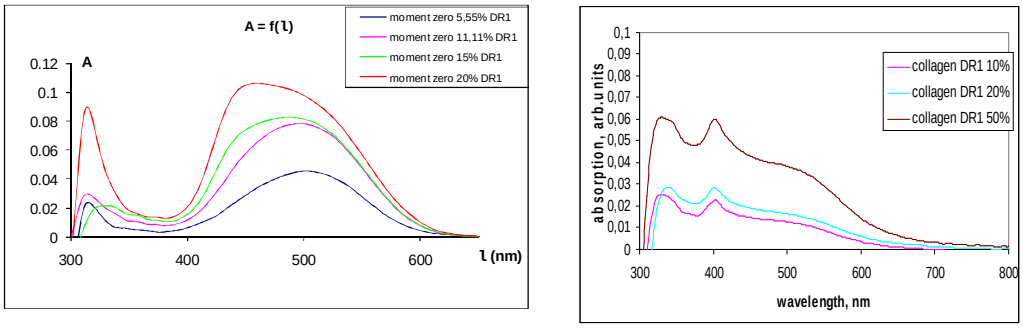
(a) (b)

Fig. 5. Concentration variation of optical absorption spectra for Rh6G in DNA-CTMA (a), DNA (b) and in collagen (c).



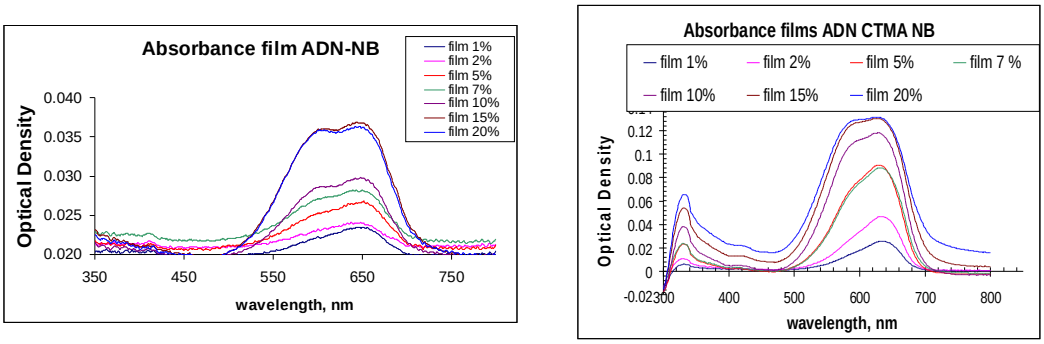
(a) (b)

Fig. 6. Concentration variation of optical absorption spectra of LDS (a) and DCM (b) in DNA matrix



(a) (b)

Fig. 7. Concentration variation of optical absorption spectra for DR1 chromophore in DNA-CTMA (a) and in collagen (b).



(a) (b)

Fig. 8. Concentration variation of optical absorption spectra for Nile Blue chromophore in DNA (a) and in DNA-CTMA (b).

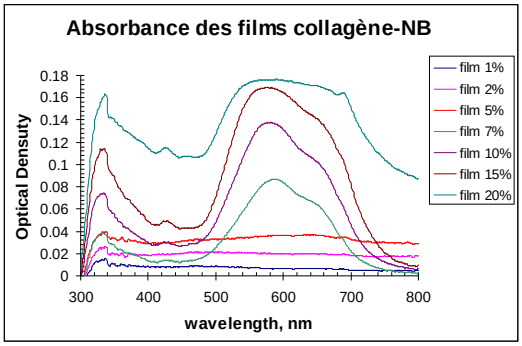


Fig. 9. Concentration variation of optical absorption spectra for Nile Blue chromophore in collagen.

IV. Photo- and thermal stability of functionalized DNA

As already mentioned the thermal stability of thin films were studied by observing the temporal variation of optical absorption spectra at room temperature, at elevated temperature (85 ^{0}C), or under UV irradiation by monitoring the optical variation of absorption spectrum.

The thermal and photodegradation studies were performed on DNA, DNA-CTMA and collagen doped with Rhodamine 590, Rhodamine 610, Disperse Red 1 (DR1), Nile Blue. For the photodegradation studies the UVA (365 nm) and UVB (312 nm) sources (Vilber Lourmat) were used.

The guest-host systems at different concentrations of dye molecules were made in water solution for DNA and collagen as matrix. In the case of DNA-CTMA complexes, known to be insoluble in water but soluble in common organic solvents, butanol was used as solvent.

We have doped also collagen with poly ethylene glycol (PEG). This was done in view of thermal crosslinking of the system. This property can be very useful for stabilizing the polar order of NLO active molecules for application in devices based on second order NLO properties (SHG, EOM, THZ generation, etc).

The kinetics of temporal degradation of a compound is usually described by the first order law:

$$\frac{dc}{dt} = -kc \qquad (1)$$

where c is the concentration of active species and k is the degradation constant.

It means that the concentration varies as

$$c(t) = c(t=0)e^{-kt} \qquad (2)$$

where c(t) is the initial concentration of absorbing species.

On the other hand, as it follows from the Lambert – Beer's law, the optical absorption of a medium is proportional to the concentration c of absorbing species. The temporal variation of the optical absorption can be represented by the temporal variation of the optical density (absorbance) A(t) at the maximum absorption wavelength. Thus Eq. (2) can be rewritten as follows

$$A(t) = A(t=0)e^{-kt} \qquad (3)$$

where A(t=0) is initial optical density.

The kinetic degradation constant can be obtained from linear regression of measured temporal variation of optical density (Eq. (3))

$$\ln A(t) = -k\,t + \text{const} \qquad (4)$$

Sometimes several phenomena contribute to the material degradation. In that case the degradation process is described by several degradation kinetics constants: k_1, k_2, k_3, …. They can be determined by fitting the temporal variation of the optical density A(t) by two, or more exponential functions

$$A(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_3 e^{-k_3 t} + ... \quad (5)$$

with

$$A_1 + A_2 + A_3 + ... = A(t = 0) \quad (6)$$

Films of DNA, DNA-CTMA and collagen, doped with the Rhodamine 610 chromophore, with their different concentrations, exhibit an excellent stability at room temperature. Within the experimental accuracy no modification of the optical absorption was observed during 40 days. A measurable degradation was observed for NB in DNA-CTMA matrix, as seen in Table 1. As NB is an ionic compound (cf. Fig. 2) a chemical reaction takes place with DNA and collagen molecules. This possibility is presently under a systematic study.

Table 1. Room temperature chemical degradation constants k_1 (day^{-1}) for Nile Blue in different matrices.

Dye concentration	DNA-NB	DNA-CTMA-NB	collagene-NB
1%		0,0009	
2%		0,0028	
5%		0,0018	
7%		0,0012	0,0006
10%		0,001	0,0004
15%		0,0009	0,0005
20%		0,0023	

In order to accelerate the degradation the films were heated to 85 ^{0}C and the optical absorption spectra were monitored as function of time. Similar experiments were done using the UV light to degrade the films at room temperature.

IV.1. Thermal degradation of thin films.

As already mentioned the thermal stability of thin films was studied by monitoring the temporal variation of optical absorption spectra at room temperature and at elevated temperature (85 ^{0}C). The photostability of chromophores were studied by monitoring the optical variation of absorption spectrum under UV illumination.

The thermal and photodegradation studies were performed on DNA and collagen doped with Rhodamine 590, Rhodamine 610, Disperse Red 1 (DR1). It was found that DNA matrix enhanced significantly fluorescence of Rhodamine 590. The chemical structures of these chromophores are shown in Fig. 2. The first and second chromophores are the well known photoluminescent dye for application in dye lasers and in organic light emitting diodes (OLED's)[5]. The third chromophore is a 1D charge transfer molecule, with enhanced first hyperpolarizability, a candidate for applications in electro-optic modulators[6].

The spectroscopic studies were performed using UV – VIS spectroscopic techniques on thin films. For these purposes the JASCO UV – VIS - NIR spectrophotometer, model V 670, was used. For the photodegradation studies the UVA (365 nm) and UVB (312 nm) sources (Vilber Lourmat) were used.

An example of the temporal variation of optical absorption spectrum is shown in Fig. 10 for LDS698 in DNA-CTMA matrix. A gradual decrease of optical absorption with a slight blue shift of its maximum is observed with the heating time.

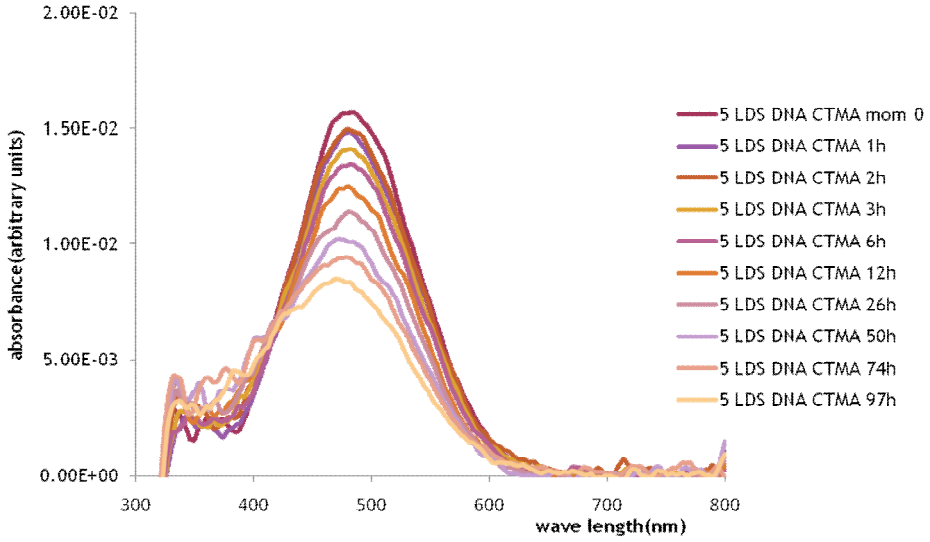
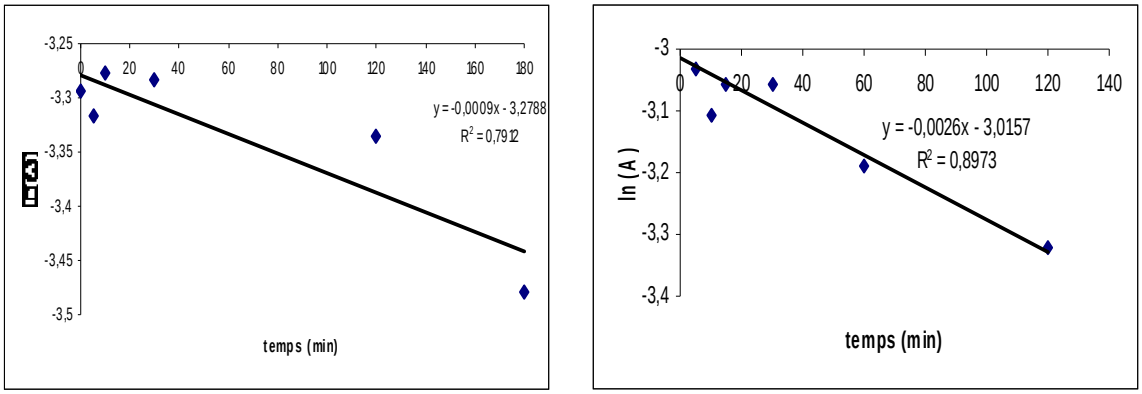


Fig. 10. Temporal variation of optical absorption spectra of LDS698 in DNA-CTMA matrix under heating at 85 ^{0}C.

The temporal variation of the optical absorption maxima for the studied samples were least square fitted by Eq. (4). Fig. 11 shows and example of such fits for NB in DNA-CTMA at 1 % (a) and 2% (b).



(a) (b)

Fig. 11. Least squares fit of Eq. (4) to experimental data for DNA-CTMA 1% NB (a) and DNA-CTMA 2% NB heated at 85 ^{0}C.

The guest-host systems at different concentrations of dye molecules were made in water solution for collagen as matrix. In the case of DNA-CTMA complexes, known to be insoluble in water but soluble in common organic solvents, butanol was used as solvent.

IV.2. Photodegradation of thin films

The photodegradation measurements were performed using a commercial Vilber Urmat apparatus with two irradiation sources: UVA at 365 nm and UVB at 312 nm. The illumination intensity was of 5.5 mW/cm^2 for UVA and 2.5 mW/cm^2 for UVB. It means that the ratio of photons illuminating the sample at UVA to that at UVB $n_{UVA}/ n_{UVB} \approx 2.6$. When illuminating with both sources the illumination time was divided by two: half at 312 nm and second half at 365 nm.

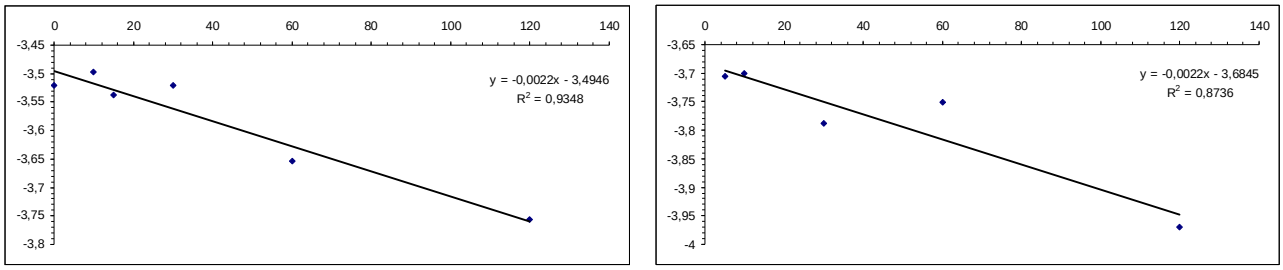


Fig. 12. Least squares fit of Eq. (4) to experimental data for DNA-Rh610 1% (a) and DNA-CTMA-Rh610 1% thin films under UV irradiation (312 nm).

As in the case of photodegradation the variation of the maximum absorbance A was least square fiited by Ea. (4) to obtain the kinetic degradation constants under the UV irradiation. Fig. 12 shows example of such a fit for DNA-Rh610 1% (a) and DNA-CTMA- Rh610 1% thin films. In both matrices the degradation constants are the same. Table 2 compares the kinetic photodegradation constants for Rh610 in DNA, DNA-CTMA and collagen in function of its concentration. A weak dependence on concentration is observed. The dye is the most stable in collagen and less in DNA-CTMA.

Table 2. Kinetic degradation constants k_1 (in min^{-1}) under UV irradiation for Rh610 in different matrices, irradiatedat 312 nm

Concentration	DNA-Rh610	DNA-CTMA_Rh610	Collagen Rh610
1%	0,0019	0,0022	0,001
2%	0,0021	0,0029	0,0009
5%	0,0014	0,002	0,0006
7%	0,0002	0,0013	0,001
15%	0,0047	0,0008	0,0013

The first order photodegradation kinetic decay constants k_1 for several other chromophores in different matrices are listed in Table 3.

Table 3. First order kinetic degradation constant k_1 ($mins^{-1}$) at room temperature and under. UV illumination (365 nm) for several studied chromophores at different chromophore concentration

Matrix	Dopant	Dopant concentration	Degradation constant k_1 (min^{-1})
DNA CTMA	NB	1%	0.0009
		7%	0.0012
		15%	0.0008
DNA	NB	1 - 20%	negligible
Collagen	NB	7%	0.0006
		15%	0.0005
DNA	Rh610	1%	0.0019
		7%	0.0002
		15 %	0.0047
DNA CTMA	Rh 610	1%	0.0022
		7%	0.0013
		15%	0.0008
Collagen	Rh 610	1%	0.001
		7%	0.001
		15%	0.0013
PMMA	Rh 610	1%	0.0005
		15%	0.0004

V. Physical properties of functionalized complexes

V1. Fluorescence

Fluorescence is one of the most important properties of organic molecules used for practical applications electronic in organic light emitting diodes (OLEDs), or more recently introduced organic light emitting field effect transistors (OLEFETs), which combine electric filed induced light emission and its electronic command and pixeling, using purely organic molecules. It was found that DNA matrix enhanced significantly fluorescence of Rhodamine 590, Rhodamine 610 and Nile Blue. The chemical structures of these chromophores are shown in Fig. 2. The first chromophore is a well known photoluminescent dye for application in dye lasers and in organic light emitting diodes (OLED's)[7]. The

second chromophore is a 1D charge transfer molecule, with enhanced first hyperpolarizability, a candidate for applications in electro-optic modulators[8].

The fluorescence measurements were performed using JASCO fluorimeter model FP 6500. All measurements were done at room temperature. It is well known that the fluorescence depends strongly on molecule environment and intermolecular interactions. In some cases it can be even quenched. However, as it was reported by several researchers the ionic environment of DNA leads to the significant increase of quantum efficiency. The observed fluorescence spectra of studied complexes are displayed in Figs. 13 - 23. They were obtained in thin films and in solutions.

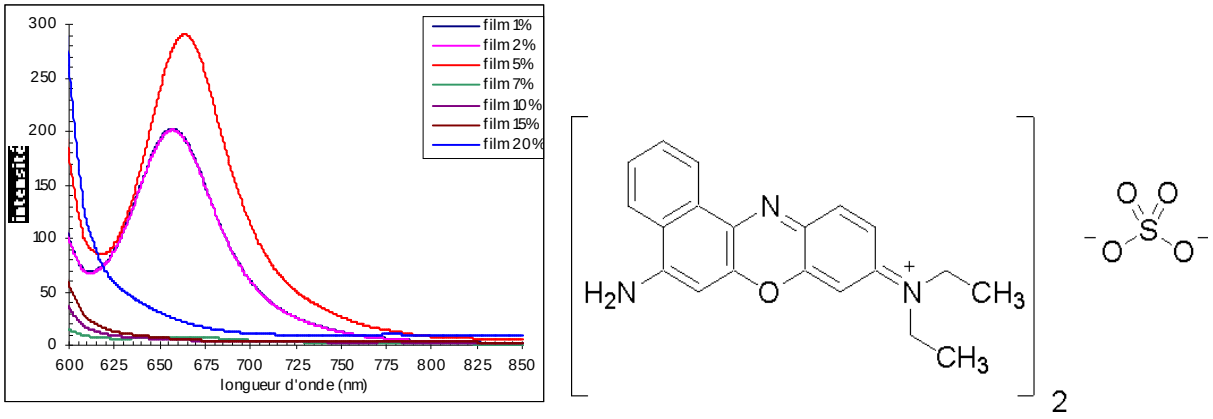
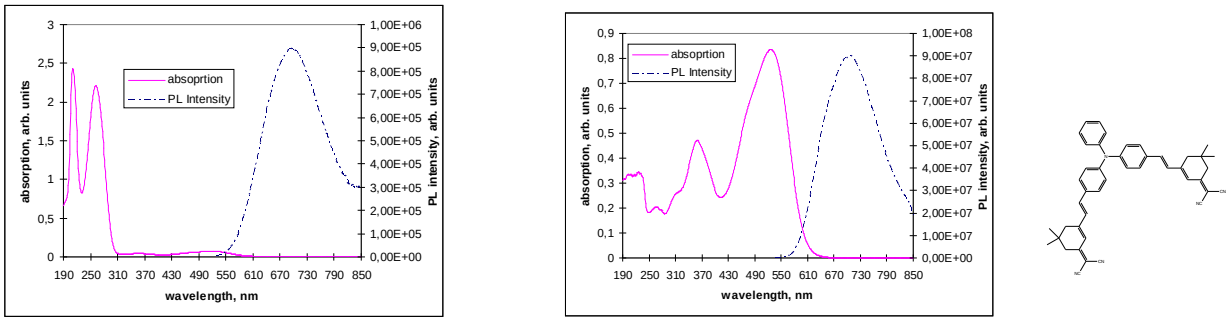
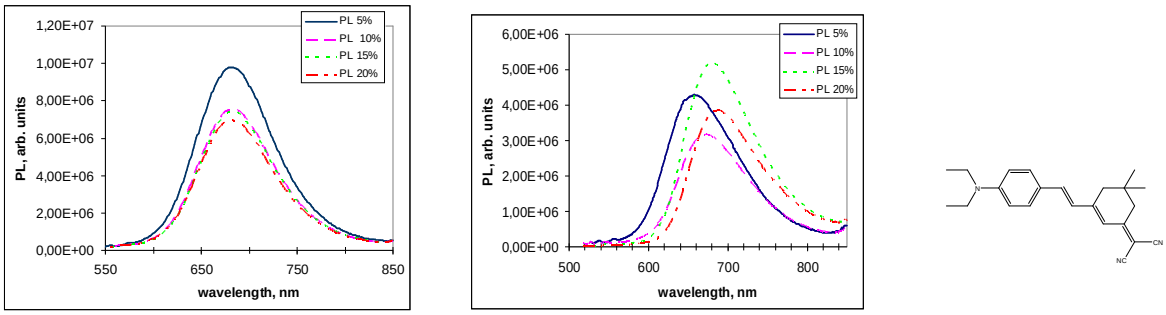


Fig. 13. Fluorescence spectra of thin films of NB chromophore in collagen matrix for different chromophore concentrations.



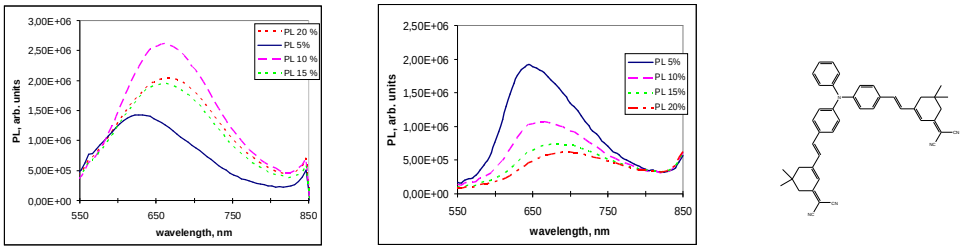
(a) **(b)**

Fig. 14. Solution optical absorption and fluorescence spectra of ENS chromophore in DNA-CTMA (a) and PMMA (b) matrices, respectively



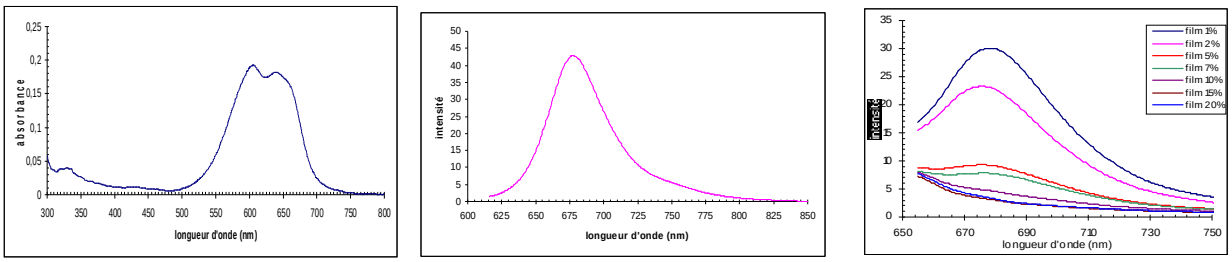
(a) **(b)**

Fig. 15. Thin film concentration variation of fluorescence spectra of DCM chromophore in DNA-CTMA (a) and PMMA (b) matrices, respectively



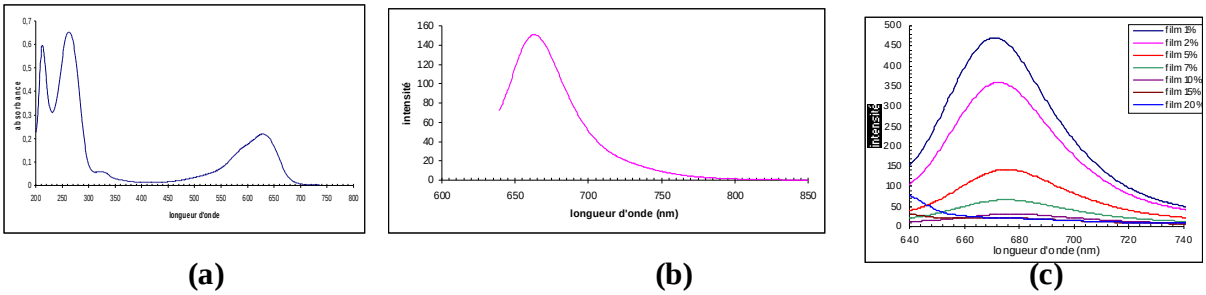
(a) **(b)**

Fig. 16. Thin film concentration variation of fluorescence spectra of ENS chromophore in DNA-CTMA (a) and PMMA (b) matrices, respectively



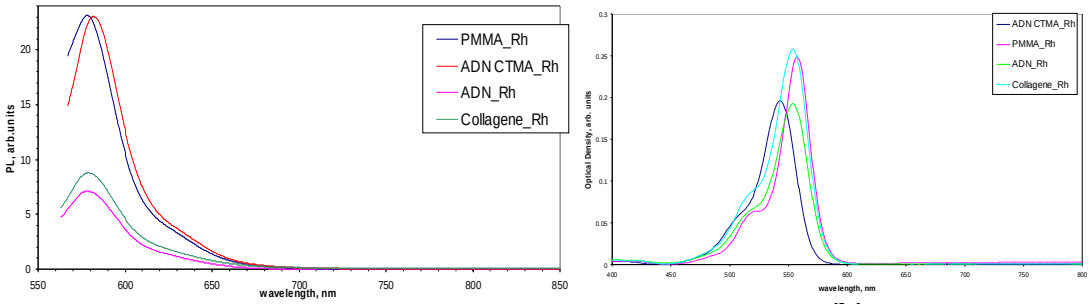
(a) **(b)** **(c)**

Fig. 17. Absorption (a) and fluorescence (b) spectra of NB chromophore in water solutions in DNA matrix and fluorescence spectrum of DNA-NB thin film (c), respectively.



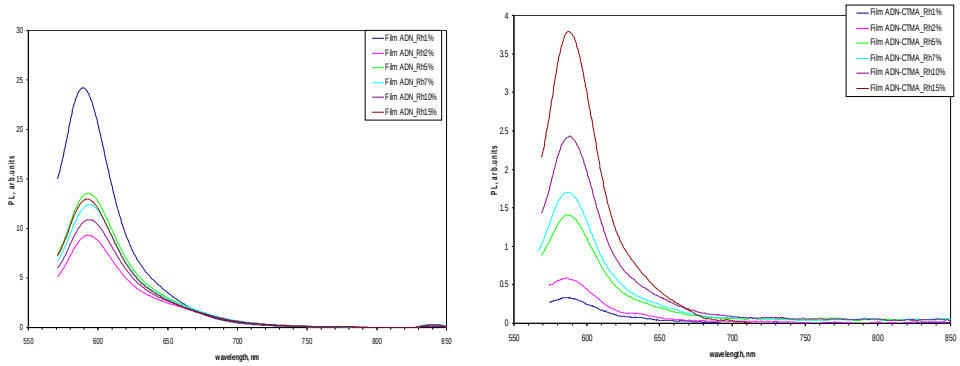
(a) **(b)** **(c)**

Fig. 18. Absorption (a) and fluorescence (b) spectra of NB chromophore in butanol solutions in DNA – CTMA matrix and fluorescence spectrum of DNA-CTMA-NB thin film (c), respectively.



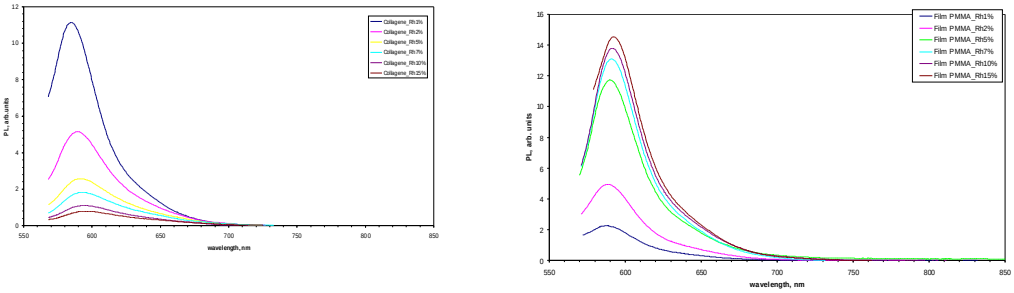
(a) **(b)**

Fig. 19. Fluorescence spectra of solutions of Rh610 (a)and absorption spectra (b) in different matrices



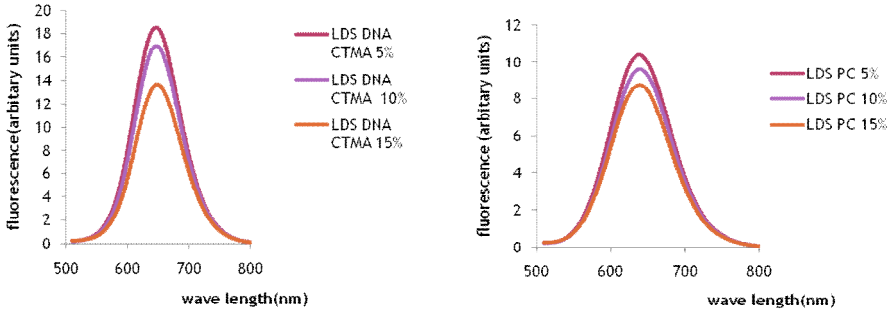
(a) (b)

Fig. 20. Thin film fluorescence spectra of DNA-Rh610 (a) and DNA-CTMA-Rh610 (b) as function of chromophore concentration.



(a) (b)

Fig. 21. Thin film fluorescence spectra of collagen-Rh610 (a) and PMMA-Rh610 (b) as function of chromophore concentration.



(a) **(b)**

Fig. 22. Thin film fluorescence spectra of DNA-CTMA-LDS698 (a) and PC-LDS698 (b) as function of chromophore concentration.

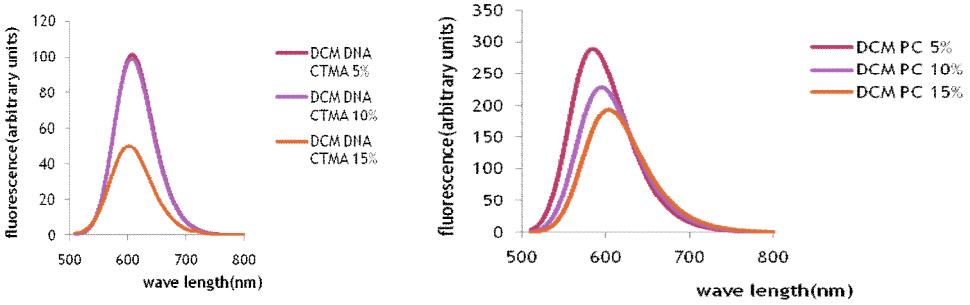


Fig. 23. Thin film fluorescence spectra of DNA-CTMA-DCM (a) and PC-DCM (b) at different chromophore concentrations.

In all cases we observe fluorescence. Howeever its behaviour with concentration depends strongly on the matrix. E.g. in PC the fluorescence is decreasing with concentration, as it is usually the case and is due to the aggregation (cf. Fig. 23). In DNA-CTMA fluorescence is increasing with concentration. This is due to the specific double strand chiral structure of DNA and is favourable for practical application.

V2. Conductivity

The conductivity experiments as well as the applications of DNA in electrochromic windows were performed in collaboration with the team of Prof. A. Pawlicka from Sao Paulo University at Sao Carlos, Brazil. DNA was used as electrolyte. It was additionally doped with lithium perchlorate and with glycerol. Lithium perchlorate increases the ionic conductivity whereas glycerol is used as plasticizer. Figure 24 shows an example of the DNA conductivity dependence on the doping molecules. The highest conductivity is obtained when doping DNA is doped simultaneously with glycerol and $LiClO^{-}_{4}$. Without lithium perchlorate the conductivity is smaller. The observed behaviour shows a that the conductivity of this biopolymer can be tailored for targeted applications by the choice of appropriate dopants. Presently we are using conducting polymers which still increase the ionic conductivity of DNA.

Another important property of DNA as polyelectrolyte that it can be used as solid material. It presents a technologically immense advantage over th usually used liquid electrolytes.

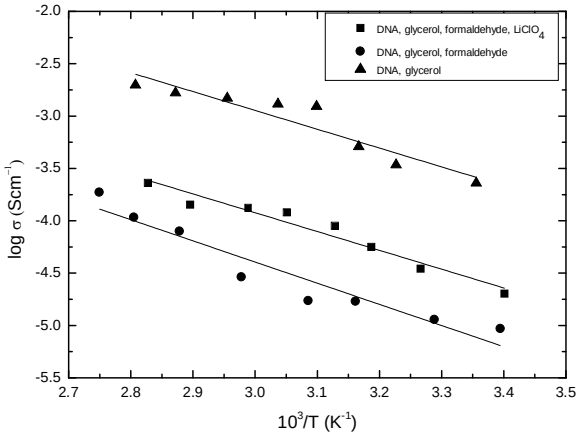


Fig. 24. Arrhenius plot for DNA-based electrolytes for samples plasticized with glycerol: DNA:glycerol A (▲), DNA:glycerol+formaldehyde (*),DNA:glycerol+formaldehyde (■).

V. Electrochromic applications

DNA is an ionic liquid. Therefore one of the possible application, exploiting this property, are smart windows, i.e. windows which change their light transmission upon application of electric field. Such smart windows find numerous applications, in aircrafts for pilotes protection against , in cars, for the same type of applications as well as for application in rear mirrors and in The electrochromic cells are used not only for the characterization of these molecular and inorganic species, but find also wide practical applications in optical switches, the so called smart windows with controllable transmission, in photovoltaic cells (so called Grätzel cells [[9],[10]]) for solar energy conversion, multicolor displays, in dimming of rear mirrors in cars, pilot protection in aircraft against dazzling by sun light, electronically driven attenuators and in transmission controllable sunglasses. A typical structure of an electrochromic cell is shown in Fig. 25. The active medium is kept between two transparent electrodes (usually ITO) and the space between is filled with an ionic conductor to transport charges from one to another electrode. The active electrochromic molecule (or compound) is either dissolved in the electrolyte or deposited on one (or two) electrodes, as shown in Fig. 25. The change of the oxidation level of the active material by electric charges leads to the change of its absorption spectrum, or in other words to a change of its color. However in most cases the electrolyte used is in liquid phase, what complicates technological process in the fabrication of such cells and their maintenance. Therefore a very interesting alternative to liquid cells represent solid electrolytes, which can be easily incorporated in the layered structure of the electrochromic cells, between the two electrodes (cf. Fig. 25).

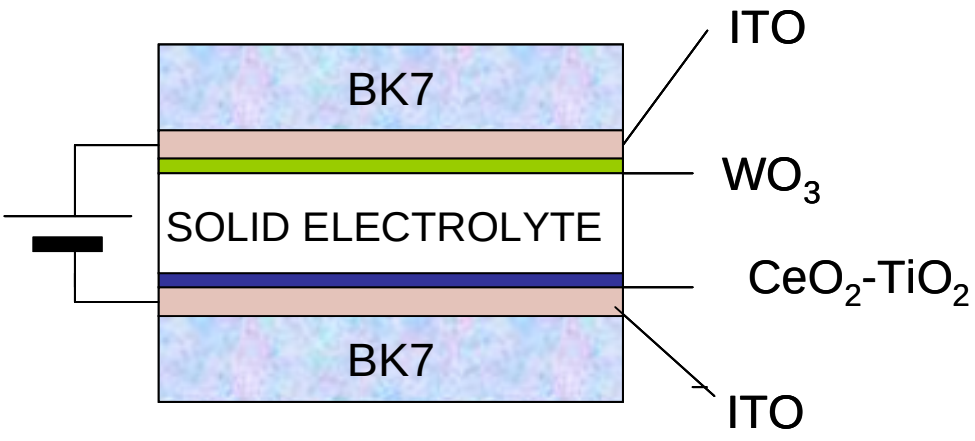


Fig. 25. Structure of the used electrochromic cell

Figure 26 shows photographs of the action of such a cell. When no electric field is applied (bleached state) the cell is almost transparent (Fig. 26 (a)). Applying electric field to ITO electrodes leads to its coloration, thus a decreas of transmittance (Fig. 26 (b)). The advantage of using DNA as electrolyte, is as already mentioned, its solid state and its large transparency.

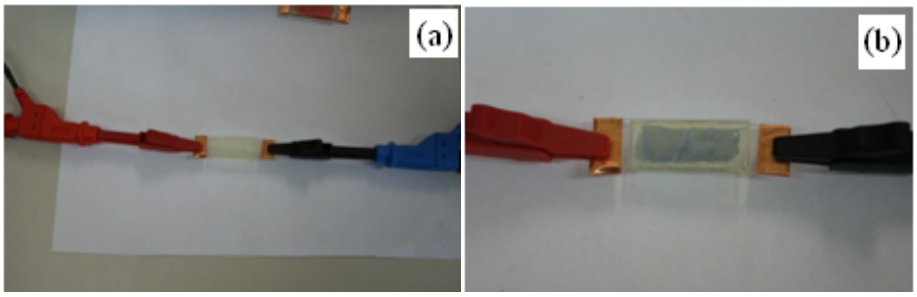


Fig. 26. Photographs of DNA-based electrolyte electrochromic cell in bleached (a) and in colored state (b).

VII. Optical damage threshold

Another important parameter determining the utility of materials in photonics is the optical damage threshold. This was measured on thin films by using a Q switched Nd:YAG laser operating at 1.064 μm fundamental wavelength, with 5 ns pulse duration and 10 Hz operating frequency. The used experimental set up is shown in Fig. 27. A set of two polarizers was used to control in a continous way by rotating one with respect to the other one. The studied films were deposited on BK7 glass substrates. The laser power was increased up to the appearance of damage to the studied film. The actual laser power was measured with Gentec Solo 2 laser & energy power meter

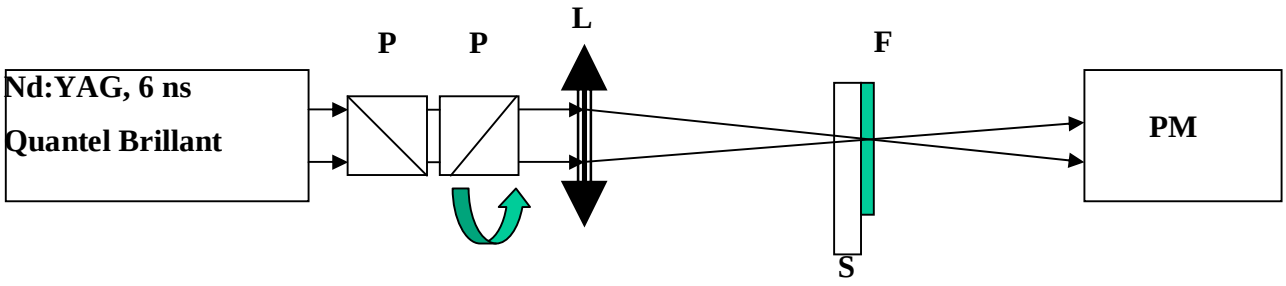


Fig. 27. Schematic representation of experimental set up for optical damage threshold measurements P – polarizers, L – focusing lens, F – the studied thin film, PM – laser power meter.

Figure 28 shows microscope images of laser beam impacts on a DNA-CTMA thin film. The measurements were done on pure collagen, DNA, DNA-CTMA complex, doped DNA-CTMA-DR1 (5, 10 and 20% doping levels) and for the sake of comparison on two synthetic polymers: polycarbonate and polyethylene glycol

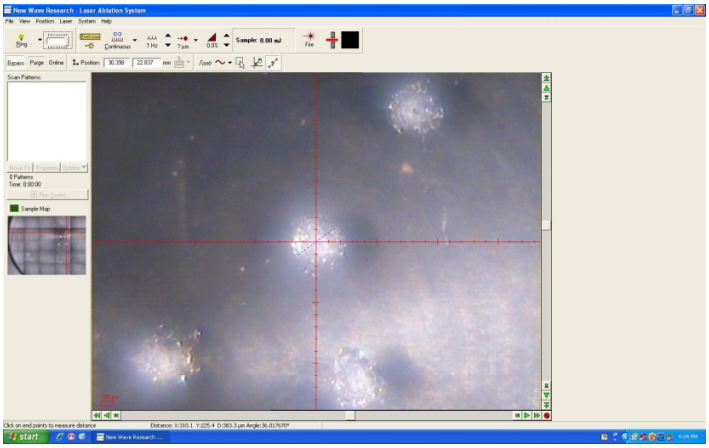


Fig. 28. Microscope images of laser beam impacts on a DNA-CTMA thin film.

Table 4. Optical damage threshold for studied thin films

Film composition	Damage threshold (W/m^2)	Damage threshold (GW/cm^2)
DNA-CTMA-DR1 5%	$3.337x10^{13}$	3.337
DNA-CTMA-DR1 10%	$3.618x10^{13}$	3.618
DNA-CTMA-DR1 20%	$4.792x10^{13}$	4.792
DNA-CTMA	$5.191x10^{13}$	5.191
DNA	$5.265x10^{13}$	5.265
Collagen	$4.139x10^{13}$	4.139
PC	$2.981x10^{13}$	2.981
PEG	$7.81x10^{13}$	7.81

The damage thresholds for DNA, DNA-CTMA, DNA-CTMA – DR1 (5%,10% and 20 w%) are listed and compared with the values measured for synthetic polymers, such as PC and PEG in Table 28. It is seen that the damage threshold for studied biopolymers, an important parameter determing applicability of these materials in photonic devices, is about two times larger than for synthetic polymers, already reputed as having very large damage thresholds.

IV. Conclusions

A series of functionalized DNA and collagen based biopolymers were functionalized and characterized for optical absorbance, photo-thermal stability, fluorescence, conductivity and optical damage.
From the present study the following conclusions can be drawn:

1. The electronic structure of active chromophores, as observed from absorption spectra depends on the matrix used and are fingers points of interaction with it.
2. The concentration level at which aggregation occurs is higher in DNA and DNA-CTMA as in synthetic polymers, as evidenced from concentration dependence of optical absorption and fluorescence spectra.
3. Nile Blue appears to be a very interesting chromophore to functionalize DNA, DNA-CTMA and collagen. Most likely it is bonded to the biopolymers. This point requires a further study
4. The studied functionalized complexes exhibit very good chemical stability at room temperature
5. DNA appears also to be a very interesting solid electrolyte for application in electrochromic and photovoltaic cells. It offers, when functionalized, good inonic conductivity values, which can be tailored depending on dopants used. Its application in smart window was demonstrated
6. The damage thresholds of thin films of the studied biopolymers: DNA, DNA-CTMA and collagen are very high and about two times larger measured for synthetic polymers, already reputed as having very large damage thresholds.

The following publications issue from this project:

1. A. Firmino, J. G. Grote, F. Kajzar, I. Rau and A. Pawlicka, Application of DNA in electrochromic cells with switchable transmission, Nonl. Opt. Quant. Opt., in print
2. A. Firmino, J. G. Grote, F. Kajzar , J.-C. M'Peco, A. Pawlicka, Novel DNA-based ionic conducting membranes, J. Appl. Phys., submitted
3. A. Pawlicka, F.Sentanin, A. Firmino, J. G. Grote, F. Kajzar and I. Rau, Ionically conducting DNA-based membranes for eletrochromic devices, Synth. Meth., submitted
4. I. Rau, O. Krupka, J. G. Grote and F. Kajzar, Nonlinear Optical Properties of functionalized DNA, Nonl. Opt. Quant. Opt., in print

List of Symbols, Abbreviations, and Acronyms

A - optical density (absorbance)

BA - benzalkonium chloride

CTMA – hexadecyltrimetylammonium chloride

DCM - [2-[2-[4-(dimethylamino)phenyl]ethenyl]-6-methyl-4H- pyran-4-ylidene]-propanedinitril

DNA - deoxyribonucleic acid

DR1 – disperse red #1

EOM – electro-optic modulation

LDS698 - [2-[4-[4-(dimethylamino)phenyl]-1,3-butadienyl]-1-ethylpyridinium monoperchlorate; Pyridine 1

NB – nile blue

NIR – near infrared light

OLED – organic light emitting diode

OLEFET - organic light emitting field effect transistors (OLEFETs)

PC - polycarbonate

PEG – poly ethylene glycol

Rh590 – rhodamine 590

Rh610 – rhodamine 610

SHG – second harmonic generation

THZ – Tetra Hertz

UV – ultraviolet light

VIS – visible light

List of Figures (If more than five figures and tables)

Fig. 28. Microscope images of laser beam impacts on a DNA-CTMA thin film.

List of Tables

Summary

Biopolymers DNA and collagen were studied for their practical applications in biotronics (photonics and electronics). They were functionalized with optically active chromophores. Additionally DNA-CTMA complexes is known for excellent optical properties and solubility in other solvents than water, the only solvent of DNA. Thermal and photodegradation of thin films of two biopolymers and the stability of chromophores embedded in were studied at room and elevated (85 °C) temperatures as well as under UV irradiation. Thin films were obtained by spin coating of corresponding solutions on glass substrates. Fluorescence of active molecules was also studied in function of matrix and fluorophore concentration. The optical damage threshold for several systems was also determined and it was found to be larger than in synthetic chromophores. Practical application of DNA as a solid polyelectrolyte was demonstrated in smart window structure.

References

[1] James G. Grote, Naoya Ogata, Damell E. Diggs and F. Kenneth Hopkins Deoxyribonucleic acid (DNA) cladding layers for nonlinear optic polymer based electro-optic devices, James G. Grote, Toshikuni Kaino, Editors, Proceed. SPIE Vol. 4991, 621 (2003)

[2] J. G. Grote, J. A. Hagen, J. S. Zetts, R. L. Nelson, D. E. Diggs, M. O. Stone, P. P. Yaney, E. Heckman, C. Zhang, W. H. Steier, A. K.-Y. Jen, L. R. Dalton, N. Ogata, M. J. Curley, S. J. Clarson and F. K. Hopkins, J. Phys. Chem. B 108, (2004), 8584

[3] B. Singh, N.S. Sariciftci, J.G. Grote, F.K.Hopkins, J. Appl. Phys., 100, (2006), 024514

[4] Z. Yu, W. Li, J. A. Hagen, Y. Zhou, D. Klotzkin, J. G. Grote, A. J. Steckl, Appl. Optics, 46, 1507(2007)

[5] J. A. Hagen, Enhanced Luminous Efficiency and Brightness using DNA Electron Blocking Layers in Bio-Organic Light Emitting Diodes, PhD thesis, Univ. of Cincinati, Cincinati, Ohio, USA, 2006

[6] E. M. Heckman, The Development of an All – DNA - Based Electro-optic Waveguide Modulator, PhD Thesis, University of Dayton, Dayton, Ohio, USA, 2006

[7] J. A. Hagen, Enhanced Luminous Efficiency and Brightness using DNA Electron Blocking Layers in Bio-Organic Light Emitting Diodes, PhD thesis, Univ. of Cincinati, Cincinati, Ohio, USA, 2006

[8] E. M. Heckman, The Development of an All – DNA - Based Electro-optic Waveguide Modulator, PhD Thesis, University of Dayton, Dayton, Ohio, USA, 2006

[9]O'Regan B. and Grätzel M., A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. Nature 353 (6346): 737–740 (1991).

[10] Grätzel M, Dye-sensitized solar cells, *J. Photochem. Photobioll C: Photochem. Reviews,* 4: 145 (2003).